Canada Alberta

FOREST RESOURCE DEVELOPMENT AGREEMENT
ENTENTE SUR LA MISE EN VALEUR DES RESSOURCES FORESTIERES

Canada Alberta

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The Canada-Alberta Forest Resource Development Agreement is a subsidiary agreement of the Canada-Alberta Economic and Regional Development Agreement, which provides coordination and cooperation between the governments of Alberta and Canada in areas of Alberta's economic development.

The Canada-Alberta Forest Resource Development Agreement is funded equally by the governments of Canada and Alberta, from April 1, 1984, to March 31, 1989.

Its primary objectives are to ensure the long-term availability of timber supplies; to optimize timber uses; and to contribute to the growth and diversification of Alberta's economy.

The Agreement comprises three programs: Reforestation; Applied research, technology transfer and opportunity identification; and Public information, evaluation and administration. These programs are managed by a joint Directorate and are implemented by the Canadian Forestry Service and the Alberta Forest Service.

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Ses objectifs principaux sont assurer la disponibilité à long terme de réserves de bois; optimiser leur utilisation; et contribuer à la croissance et la diversification de l'économie de la province.

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REVIEW OF CHEMICAL PRODUCTS PRODUCED FROM THE TIGNEY EXPLODED ASPENWOOD PROCESS

Arbokem Inc.[1]
1986

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and the Alberta Forest Service pursuant to the
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DISCLAIMER

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The views, conclusions, and recommendations are those of the authors. The exclusion of certain manufactured products does not necessarily imply disapproval nor does the mention of other products necessarily imply endorsement by the Canadian Forestry Service or the Alberta Forest Service.

As a reference, the study "The Tigney Steam Explosion Process-Experiences from Europe" by Ingemar Croon and Per Jerkeman

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has a complementary views, conclusions and recommendations and is available as indicated below.

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ABSTRACT

A review of available information on the characteristics and technical performance of the Tigney cellulose and lignin products has been completed. The steam-explosion process is capable of producing only contaminated fractions of cellulose, hemicellulose and lignin.

The quality of the Tigney cellulose was concluded to be unsatisfactory for the preparation of viscose, acetate or microcrystalline products. It is unlikely that the Tigney cellulose of the present quality could displace conventional dissolving pulp for these end uses. The chemical reactivity of the Tigney lignin was noted to be low. The Tigney lignin product has been tested to be unacceptable for use as direct substitute for phenol-formaldehyde resin for panelboards, bridging agent for methanol-diesel fuel mixture and drilling mud additive.

The addition of any subsequent purification steps would only increase the immense complexity of the concept of producing low-cost (valuable) chemical products from aspen wood. The economic viability is dependent, to a large extent, on the successful marketing of many wood-derived products simultaneously.

SUMMARY

Background

Under the aegis of the Alberta Forest Service, Tigney Technology Inc. constructed and operated a pilot plant to demonstrate its proprietary steam-explosion process. Aspen wood was to be separated by this means into three major constituents: cellulose, hemicellulose and lignin. The cellulose produced was intended for use in place of conventional dissolving pulp for viscose, acetate and microcrystalline cellulose production. The lignin product was intended primarily as a substitute for conventional phenol-formaldehyde resin in the panel board industry. In early 1986, the Alberta Forest Service contracted several external expert groups to evaluate the characteristics and technical performance of the Tigney cellulose and lignin products.

Objective

The objective of the present work was to review all available information on the characteristics and technical performance of the Tigney cellulose and lignin products. Specifically, answers are sought to the following questions:

a) How do the Tigney cellulose and lignin products fit into the commercial market?

b) Is there any basis for continuing the development of the Tigney technology at the pilot-plant demonstration scale?

Results

A detailed review of available information on the Tigney technology and its cellulose and lignin products have been completed. The major conclusions are as follows:

1. The steam-explosion process is capable of producing only impure fractions of cellulose, hemicellulose and lignin. Because of the nature of wood/wood components and of the Tigney (or any other similar) process, optimization of operating conditions to produce three "pure" fractions concurrently is not possible.

2. The quality of the Tigney cellulose was concluded to be unsatisfactory for the preparation of viscose, acetate or microcrystalline products. It is unlikely that the Tigney cellulose in its present quality could displace conventional dissolving pulp for these end uses.

3. The chemical reactivity of the Tigney lignin was noted to be surprisingly low. Moreover, the chemical characteristics of the Tigney lignin does not appear to be unique. It is similar to other steam-explosion (or autohydrolysis) hardwood lignin material.

4. The Tigney lignin product has been tested to be unacceptable for use as direct substitute for phenolformaldehyde resin for panelboards, bridging agent for methanol-diesel fuel mixture and drilling mud additive.

5. The addition of any subsequent purification steps would only increase the immense complexity of the concept of producing low-cost valuable chemical products from aspen wood. The economic viability is dependent, to a large extent, on the successful marketing of many wood-derived products simultaneously.

Recommendations

Tigney cellulose and lignin have not been demonstrated to meet the minimum performance of products which they are intended to replace. The prospect of success is not good on the basis of present scientific and technical evidence. Further pilot plant development work is not justified at this time.

TABLE OF CONTENTS

PAGE

ABSTRACT iii

SUMMARY v

INTRODUCTION 1

SCOPE OF WORK 2

EXPLODED-WOOD PROCESS TECHNOLOGY 2

CELLULOSE PRODUCT 9
- Bleaching Technology 9
- Cellulosic Substances 9
- Extraneous Substances 10
- Conventional Viscose Manufacture 10
- Cellulose Carbamate 12
- Cellulose Acetate Manufacture 12
- Microcrystalline Cellulose 13
- Non-Dissolving Pulp 14

NO-CELLULOSE PRODUCTS 15
- Xylose and Xylose Derivatives 17
- Lignin Material 17
- General Characteristics 17
- Diesel Fuel Additive 18
- Composite Board Adhesive 18
- Drilling Mud Application 20

PROCESS ECONOMICS 22

CONCLUSIONS 23

RECOMMENDATIONS 24

LITERATURE CITED 25

LIST OF ILLUSTRATIONS

Figure

1 Lignin solubility as affected by time and temperature of autohydrolysis

2 Operating times and temperatures cited in various patents

3 Principal elements of the Tigney pilot plant

4 Overall Tigney processing scheme

5 Consumption of formaldehyde by lignins in hydroxymethylation

LIST OF TABLES

Table

I Optimum cooking time for batch steam-explosion of hardwoods

II Comparison of selected properties of two commercial dissolving pulps with those of Tigney cellulose

III Fibre classification of Tigney cellulose

INTRODUCTION

Trembling aspen (Populus tremuloides) is the most common poplar species found in Canada (1). In Alberta, aspen accounts for over 80% of the merchantable hardwoods. This resource is currently under-utilized by the forest product industry (2). In the continuing effort to promote the use of this resource, the Alberta Government has undertaken a broad development program to explore new uses for aspen wood.

The original steam-explosion process was developed by Mason in 1925 (3,4). Many of the recent patented versions are based on this 60-year old concept. In the Masonite process, wood chips are fed into a small digester ("Masonite gun"). The charging valve is closed; high pressure steam is introduced and the temperature is rapidly brought up to about 200° C, where it is maintained for approximate 15 seconds. The softened chips are further heated to 280-285° C and the temperature kept at this level for another 4 to 5 seconds. Next, the digester content is blown under rapid decompression. Defibration takes place and the steam is separated from the fibres in a cyclone. The total cooking cycle takes less than 60 seconds to complete. This pulp has been used since 1926 to make the ubiquitous Masonite hardboard.

In the Masonite process, a widespread destruction of the pentosans takes place resulting in the evolution of furfural (5). The cellulose degree of polymerization (DP) was noted to fall off markedly. The viscosity of the resulting cellulose has been noted to be too low for use as dissolving pulp. The Masonite lignin has been reported to be thermo-plastic and soluble in various organic solvents (5). The hydrolyzates from the Masonite and similar processes have been used for many years as animal feed supplements.

Tigney Technology Inc. (Sherwood Park, Alberta) has proposed the development of a "wood chemicals" factory based on aspen as feedstock. In 1985, this project proposal was given financial support by the Alberta Government for pilot plant-scale demonstration (6).

Subsequently, a small pilot plant was designed and constructed at the Alberta Research Council (ARC) facility in Clover Bar. Tigney staff operated this pilot plant to demonstrate and optimize the manufacture of cellulose and lignin products from aspen wood. Certain quantities of Tigney cellulose and lignin were also made for further testing by the Alberta Forest Service (AFS).

In collaboration with researches at the Alberta Research Council (ARC), Tigney staff investigated the chemical and physical properties as well as several potential end uses of the steam-exploded cellulose and lignin products. Concurrently, the AFS sent samples of the Tigney cellulose and lignin products for evaluation by a selected group of technical experts in Canada, the United States and Scandinavia.

SCOPE OF WORK

In July 1986, the AFS retained Arbokem Inc. to conduct an independent review of the technical potentials of the Tigney cellulose and lignin products. The principal data base was as follows:

1) Technical reports submitted by various technical experts contracted by AFS,

2) Technical reports submitted by Tigney Technology Inc., and

3) Scientific and technical literature.

Additional information was provided from interviews with selected personnel who have either evaluated the Tigney products or who have an interest in the Tigney technology.

The present work was aimed to answer to following questions:

1) How do the Tigney cellulose and lignin products fit into the commercial market?

2) Is there any basis for continuing the development of the Tigney technology at the pilot-plant demonstration scale?

EXPLODED-WOOD PROCESS TECHNOLOGY

Aspen wood (Populus tremuloides) has an average composition of 49-51% cellulose, 20-21% hemicellulose, 17-19% lignin and 1-3% extractives (7). The aim of the generic exploded-wood process technology is to fractionate the wood into three major groups:

* Cellulose
* Lignin
* Hemicellulose

Because the "front-end" of the steam-exploded process is exceptionally simple in nature, it has continued to draw considerable interest in the forest products industry in North America as well as in Europe. The basic processing scheme involves steam heating of wood chips for a very short time at elevated temperature and pressure. After which time, the pressure is released quickly causing the wood mass to discharge from the reaction vessel under "explosion" conditions. The wood is thus hydrolyzed and defibrated (8). To a large extent, the steam-explosion process has considerable similarities to the well-established pre-hydrolysis kraft technique used for the production of dissolving pulp (3).

The basic mechanism of the steam-explosion and related processes have been investigated (9-14). Lora and Wayman (10) studied the autohydrolysis of aspen and eucalyptus at 175-220° C. These workers found that the hydrolysis of wood with steam at elevated temperature and

pressure is catalyzed by organic acids formed fr[illegible] the wood components during the hydrolysis. The chemical changes which take place include the hydrolysis of hemicelluloses to soluble sugars by operating conditions secondary reactions would occur which would result in the formation of hydroxymethylfurfural and furfural. The presence of monomeric lignin degradation products has also been reported by various researchers in autohydrolysis liquor (15,16).

In this type of hydrolysis of wood, lignin is rendered soluble in various organic solvents and dilute alkali. Wayman and co-workers (10,11) have noted that the maximum lignin solubility is varied for each combination of process time and temperature. As shown in Figure 1, short time and high temperature appear to afford the highest lignin solubility.

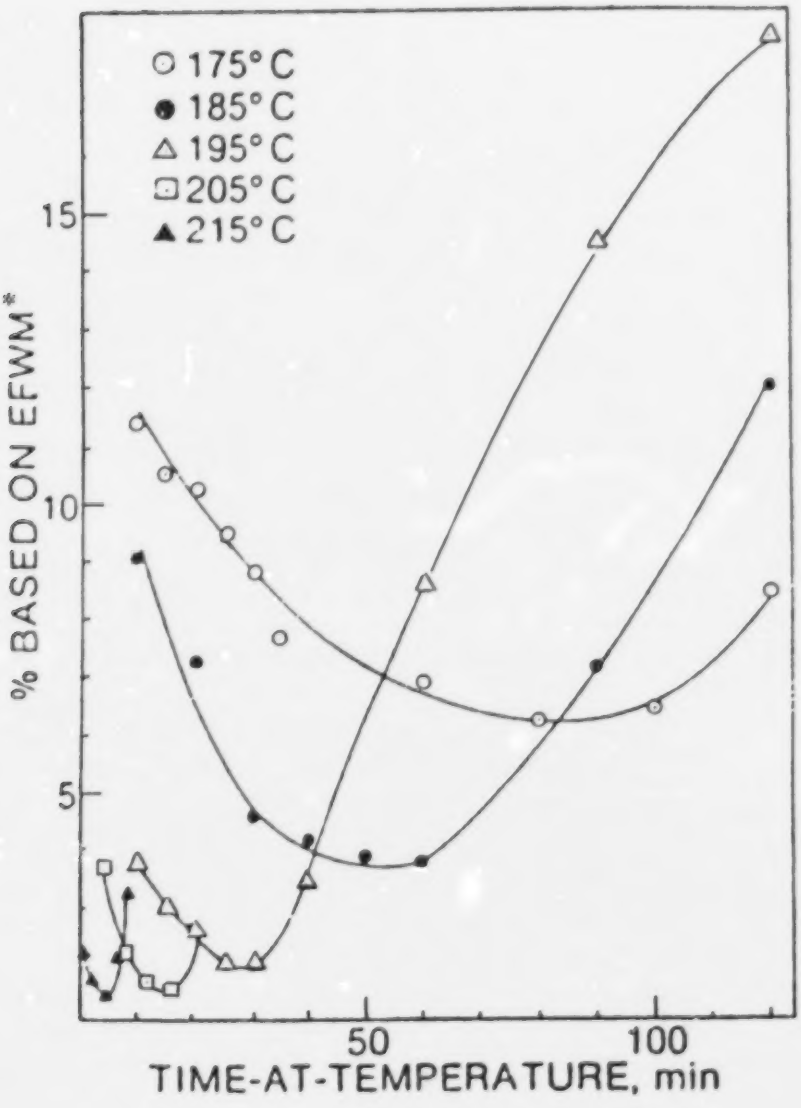
The relationship between lignin solubility and the lignin glass transition temperature is not well understood at present. At 165-185° C., lignin is known to "plasticize" such that its separation from the main fibre components is faciliated (17). At present, there is no evidence to suggest that a unique set of operating conditions would exist to effect complete separation of hemicellulose, cellulose and lignin components. Indeed, the Tigney cellulose still contains significant amount of residual lignin.

Lipinsky (8) has noted that operating conditions may be varied to optimize the production of xylose, lignin or cellulose. But viable plant economics require high yields and qualities of all main products.

The optimum cooking conditions for the steam-explosion technique have been investigated by Noble et al. in 1980 for the U.S. Dept. of Energy (8). The study showed that, among other things, if xylose yield is optimized, too much lignin would remain on the cellulose fibres. Conversely, if lignin is optimized, xylose and some of the glucose would be degraded to furfural and related compounds. Table I shows the optimum cooking time for batch steam-explosion of hardwoods.

Table I. Optimum Cooking Time for Batch Steam-Explosion of Hardwoods (8)

Product	Optimum Cooking Time, sec.
Xylose	20
Glucose	50
Glucose + Xylose	40
Rumen Digestibility	60
Lignin	120



* Lignin remaining in residue after 90% dioxane extraction of aspen (EFWM = extractives-free wood meal) autohydrolyzed with 1:1 water:wood ratio. Time and temperature refer to autohydrolysis conditions.

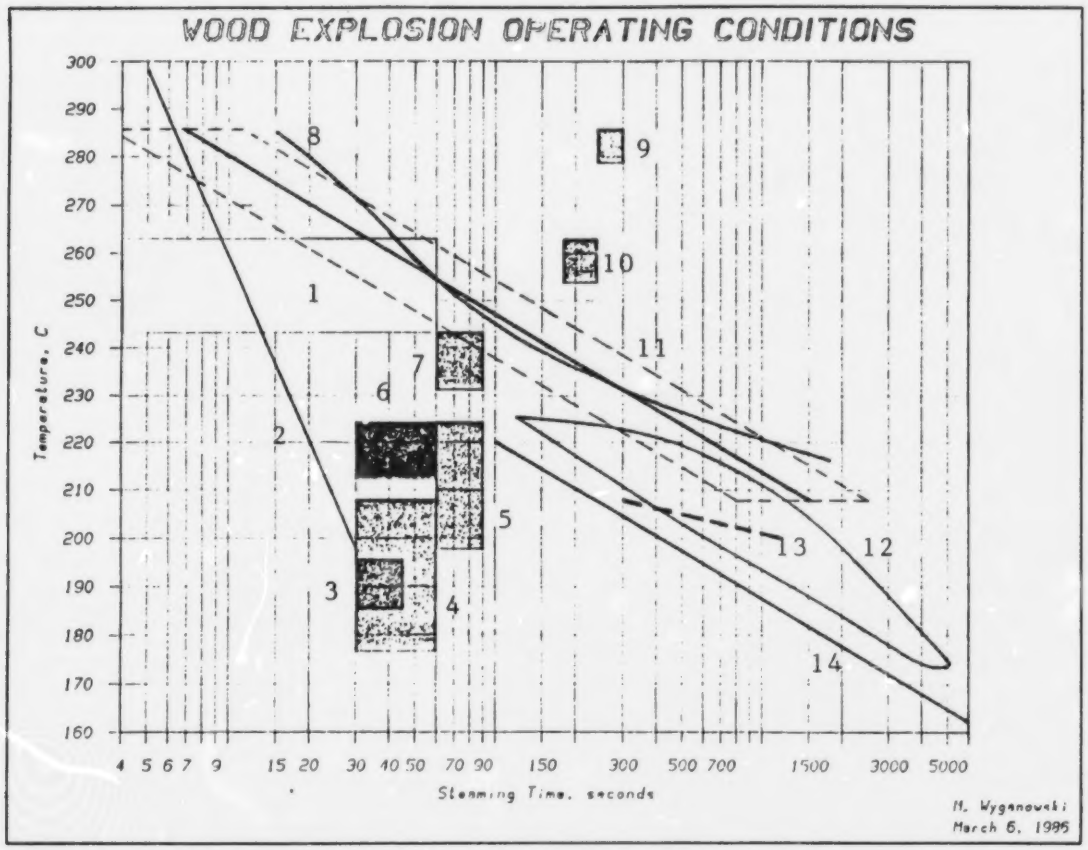
Figure 1 - Lignin solubility as affected by time and temperature of autohydrolysis [10].

Various conditions for the generic steam-explosion process have been patented during the past 15 years (6,8). Figure 2 illustrates the different over-lapping claims noted in the relevant patent literature. The initial Canadian patent (18) was issued in 1981 to Mr. E. De Long, a principal of Tigney Technology Inc. The patent was assigned to the Canadian Patent Development Ltd., a Crown corporation. More recently, an improvement patent (19) was issued to Mr. De Long disclosing the specific process technology which is currently offered by Tigney Technology Inc. There are various conflicting claims to the licensing and sub-licensing rights to the basic steam-explosion process patent (20).

The Tigney pilot plant design was essentially based on the developed by Masonite Corp. and others (4,8). Figure 3 illustrates the principal elements of the Tigney pilot plant.

Most of the experiments were made with aspen wafers (< 1 mm. thick). In the pilot plant trials, the best operating conditions established by Tigney in the pilot plant were 30-35 seconds dwell time and about 255° C (at about 612 psig pressure) (21,22). The overall Tigney processing scheme proposed (23) is shown in Figure 4.

The nominal yield figures are those given by Tigney Technology Inc. (21,23). No definitive experimental data were available to substantiate these product yields. The presence of wood extractives was not considered. Moreover, the presence of bark, oversize or undersize wood wafers, knots, etc., would certainly alter the overall product yields.



1 Tigney
2 Masonite/sugars
3 Algeo/almond hulls
4 Algeo/grain,corn,barley,cull beans
5 Algeo/alfalfa seeds
6 Masonite/board
7 Algeo/hay,straw
8 Masonite/molding
9 Algeo/coffee grounds
10 Algeo/almond shells
11 Iotech
12 Stake/lignin
13 Stake
14 Stake/cattle feed

Figure 2 - Operating Times and Temperatures Cited in Various Patents [6].

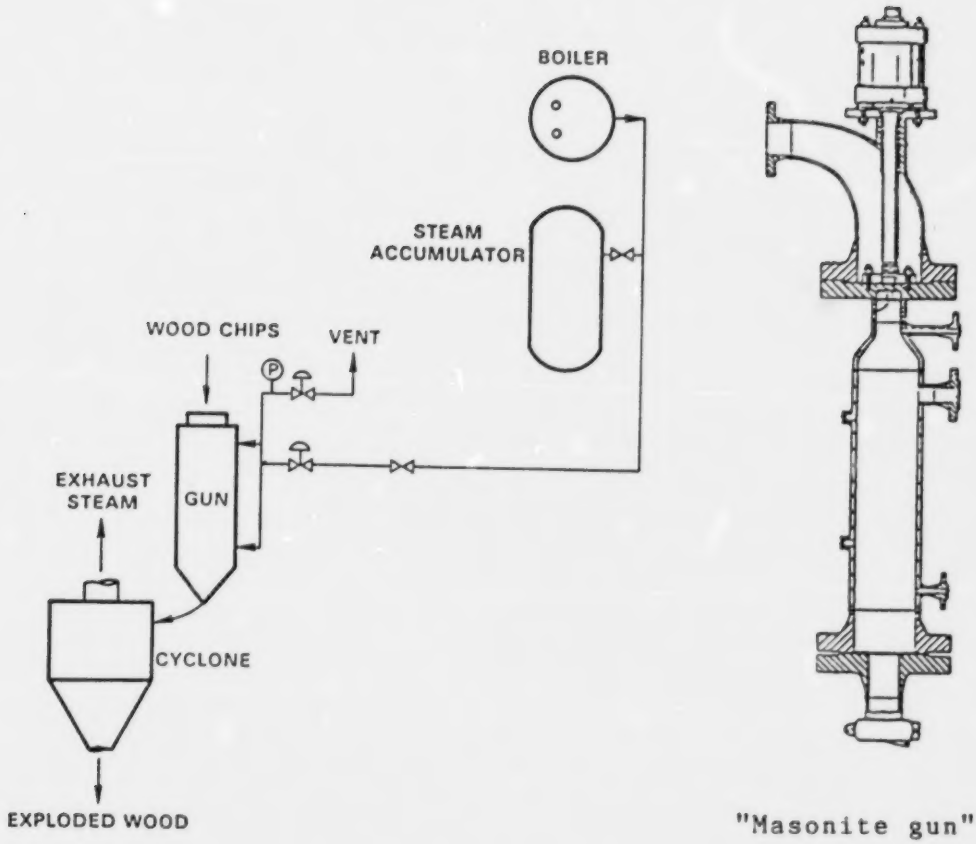


Figure 3 - Principal elements of the Tigney Pilot Plant (adapted from Ref. [8])

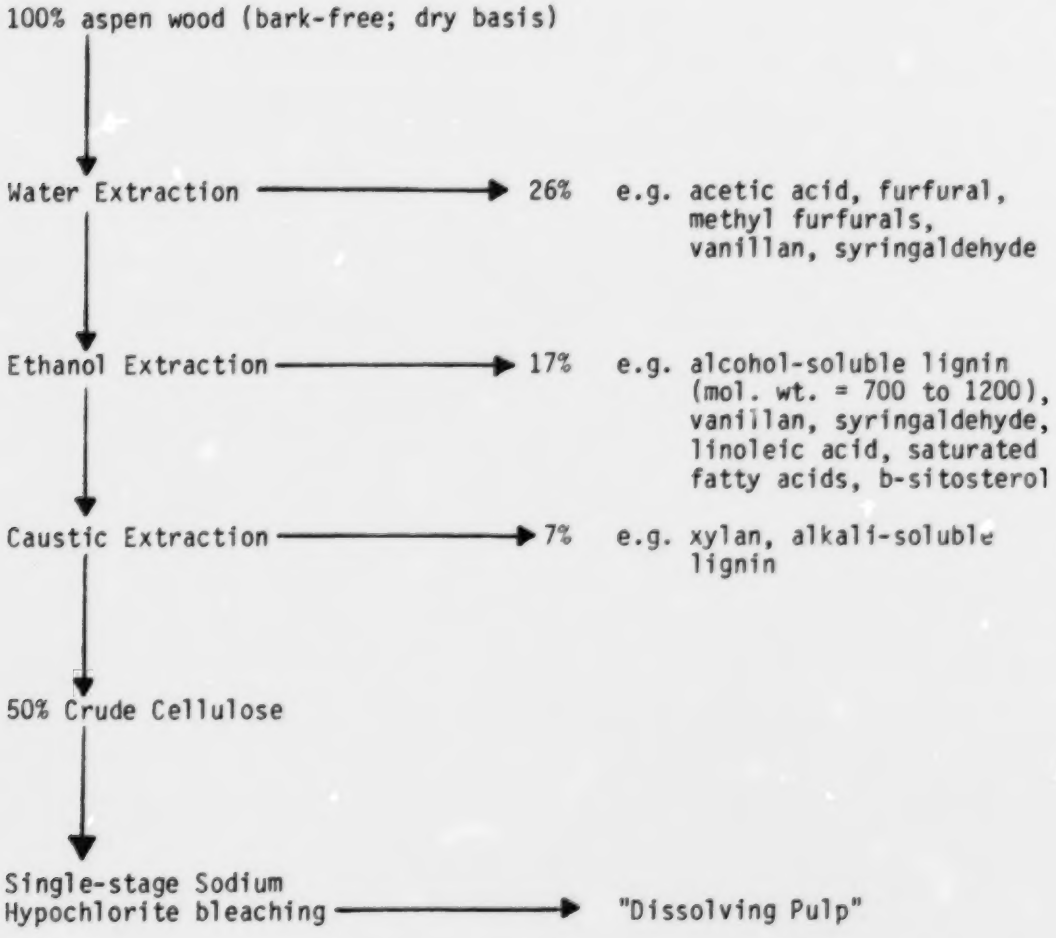

100% aspen wood (bark-free; dry basis)
Water Extraction
26%
e.g. acetic acid, furfural, methyl furfurals, vanillan, syringaldehyde
Ethanol Extraction
17%
e.g. alcohol-soluble lignin (mol. wt. = 700 to 1200), vanillan, syringaldehyde, linoleic acid, saturated fatty acids, b-sitosterol
Caustic Extraction
7%
e.g. xylan, alkali-soluble lignin
50% Crude Cellulose
Single-stage Sodium Hypochlorite bleaching
"Dissolving Pulp"

Figure 4 - Overall Tigney Processing Scheme

CELLULOSE PRODUCT

This fraction is produced from the raw Tigney pulp mass by sequential extraction with water, ethanol and dilute caustic soda solution. Tigney has recently suggested that the ethanol extraction step may be optional, depending on the requirements of the product end uses (24). The Tigney estimated yield of this fraction is about 50% based on original dry wood. The extracted product was typically bleached with NaOCl in a single stage operation (21). The brightness of the bleached product is less than 80-pts GE. This finished cellulose product has been proposed by Tigney as a direct substitute for, among other things, commercial viscose-and acetate-grade dissolving pulps.

Bleaching Technology

Hypochlorite bleaching is not a good technique for the production of high brightness pulp with low brightness reversion characteristics (25). It is well known in the technical literature that carbonyl groups are formed during hypochlorite bleaching which would lead to a finished pulp with high brightness reversion characteristics (26,27). Hypochlorite-bleached pulp normally has a yellowish cast.

Cellulosic Substances

In comparison to commercial dissolving pulp, the AS-IS finished pulp contained too much "S_{18}" (representative of hemicellulose) and "S_{10}-S_{18}" (representative of degraded cellulose) substances (29-31). These parameters are indicative of the "impure" nature of the Tigney pulp.

The alpha-cellulose of the Tigney pulp has been noted to be significantly lower (ca. 10%) than that of the customary dissolving pulp. This finding suggests that the Tigney process can only provide a cellulose-rich but not cellulose-pure fraction. The native viscosity of the Tigney cellulose has also been reported to be lower than that of commercial pulps (30). As shown in Table II, the Tigney cellulose does not compare very favourably with typical commercial dissolving pulps.

Lachenal and Monzie at the Centre Technique des Papiers in Grenoble, France have investigated the possibility of producing dissolving pulp by the steam explosion method (32). The range of processing pressure and time studied was 20 to 50 bars (294 to 735 psig) and 10 to 240 seconds, respectively. These workers found that it was not possible to obtain a cellulose residue of DP > 200, which contains less than 10% lignin. Attempts to increase processing pressure with shorter time were unsuccessful in producing a high DP cellulose with low residual lignin content. The basic problem is very similar to that cited previously by Lipinsky (8).

Table II. Comparison of selected properties of two commercial dissolving pulps with those of Tigney cellulose

	Tembec Inc. "Temsupr" *	Billerud "Alba" **	Tigney Cellulose
Alpha Cellulose, %	92.5	NT	81.2
S_{10} at 25° C, %	10.0	12.0	24.4-28.9
S_{18} at 25° C, %	5.0	7.5	7.1-13.1
S_{10}-S_{18}, %	5.0	4.5	15.8-17.3
Klason lignin, %	NT	0.1	1.8
Viscosity, cuam	2.6	NT	12.0
Deg. polymerization	NT	800	225
Copper number	NT	0.2-1.5	2.38
Ash, %	0.06	0.04	0.44-0.56
Calcium, ppm	200	60	852-2600
Copper, ppm	2	NT	108
Iron, ppm	6	4	69-282
Manganese, ppm	1	nil	0.9-33
Silicates, ppm	NT	40	50
DCM extractibles, %	NT	0.2	1.3
Ether extractibles, %	0.25	NT	0.63
Brightness, pts	94.0	91.5	76.6-77.7

Note:

* Ammonium base softwood sulphite; data from Ref. (30)
** Sodium base softwood sulphite; data from Ref. (31)
NT = not tested

Extraneous Substances

Chemical analyses made by various contractors have shown that the finished Tigney pulp contained high concentrations of lignin, ash, calcium, silica, transition metals (e.g., Mn, Fe and Co) and wood extractives (30,31,33). The presence of these substances might only be partially attributable to the quality of tap water used in the Tigney pilot-plant preparation of the cellulosic pulp. The major proportion of these extraneous substances would likely to originate from the original wood used. The post-treatment of the Tigney raw product may be too simple to effect adequate removal of these wood-originated extraneous substances from the finished cellulose.

Conventional Viscose Manufacture

Commercial dissolving pulp is routinely steeped in 18% NaOH solution to produce an alkali cellulose (29). The purpose of this step is to prepare the pulp for controlled depolymerization (through aged reaction with oxygen in the air) and for subsequent uniform reaction with CS_2.

The hydroxyl groups of the cellulose are ionized for reaction with CS_2. Cellulose is regenerated through the reaction of cellulose xanthate with dilute sulphuric acid (coagulating bath) (34).

Depolymerization is desired to provide the needed degree of polymerization (DP) for specific end uses. For example, commercial wood pulp has a DP range of 700 to 1100. In the tire cord rayon, a DP of 500-600 is required. For regular rayon and cellophane grades, a lower DP of 300-400 would be satisfactory (29).

The DP of the Tigney pulp is about 250, with a reported narrow distribution range (22). This feature would appear to be beneficial. The alkali aging step in the preparation of the viscose might thus be greatly reduced or omitted. However, this narrow range DP might be misleading. As indicated by the relatively high content of "S_{18}" material, the residual hemicelluloses might have been significant contributing components of this apparently low DP fraction.

In any case, reaction of the Tigney pulp with alkali would still be required as it is necessary to a) remove unwanted hemicelluloses and b) from alkali cellulose for subsequent xanthation (29,34,35). Furthermore, with a fixed low DP, the usefulness of the Tigney pulp would be greatly limited to perhaps only a few utility grades of viscose.

The Tigney pulp properties were tested by Tembec Inc. (30) and Saltech/STFI (31). Econotech Services Ltd. has used this finished Tigney pulp for lab scale viscose production (36). The general conclusion was that the finished Tigney pulp is unsatisfactory for the preparation of viscose using established techniques. The quality of the Tigney pulp is significantly different from that of commercial viscose-grade dissolving pulp (See also Table II).

The extraneous substances present in the Tigney pulp would cause operating problems in conventional viscose plants (29,37,41). Some of the more important detrimental effects are listed below:

High Values	Example Major Problems
S_{18}	Lower yield of viscose (from dissolution of hemicelluloses) Lower final yarn strength Reduced rate of alkali absorption by pulp
S_{10}-S_{18}	Reduced drainage of alkali cellulose slurry Reduced rate of pressing out excess alkali Lower final yarn strength (too much degraded cellulose present)
Extractives	Reduced filterability of viscose Lower spinnability of viscose
Ash	Lower filterability of viscose

The presence of transition metals has both positive and negative effects on the viscose aging process (29). For example, Co, Mn and Fe are aging accelerators (37). And Cu is an aging inhibitor (29,30). In commercial practice, the dissolving pulp contains little or no metals of this type. Specific amount and type of metal salts are normally added on purpose for a pre-determined end effect. In the Tigney pulp, the transition metal content is generally high and not regulated uniformly with the present processing scheme.

Cellulose Carbamate

This process for the production of soluble cellulose derivative was developed by Neste OY of Finland (42). The basic steps of the patented process include irradiation of the starting pulp to specific DP levels and followed by reaction with urea to form cellulose carbamate. The stable finished product is soluble in aqueous NaOH. Cellulose is regenerated through coagulation in a bath of sulphuric acid. The carbamate approach offers an interesting alternative to the classical xanthation process.

As cited by Neste personnel (43), the Tigney pulp is unsuitable because of the high contents of ash, lignin and extractives, and apparently low DP. In the Neste carbamate process, irradiation of high DP is practiced to produce precise DP in the raw material to meet specific end use requirements. In this instance, electron beam irradiation would only reduce the DP of the Tigney cellulose further. Although low DP of the Tigney pulp is not necessarily a severe disadvantage, its low value does again limit its applicability.

Cellulose Acetate Manufacture

In the acetate process, dissolving pulp is acetylated with acetic acid and sulphuric acid to form a stable derivative which is soluble in common solvents (29,34). Unlike the viscose process, the raw pulp is not afforded additional purification through an alkali pretreatment step. All cellulose and impurities take part in the acetylation reaction. Thus, the original purity in the acetate-grade pulp has to be very high. An acetate-grade dissolving pulp normally has a DP >1500 (33).

From a technical view point, if the pulp quality was unsatisfactory for viscose production, it would also be unacceptable for acetate production. For acetate applications, commercial dissolving pulp has an alpha-cellulose content of a least 92%. In contrast, the Tigney pulp has an alpha-cellulose content of about 80% (30,31). This lower quality is also reflected in the relatively high content of "S_{18}" and "S_{10}-S_{18}" substances of the Tigney pulp.

Because of the nature of conventional acetate manufacturing method, the presence of extraneous substances in the raw pulp has a large adverse effect (29,44-51).

Both Canadian Celanese (52) and Econotech (34) have tested the Tigney pulp, on a lab-scale, for acetate production. The test results indicated that the Tigney cellulose was not very reactive (poorly

acetylated), resulting in unacceptable levels of haze and false viscosity. Workers at these laboratories have thus concluded that the finished Tigney pulp would not be satisfactory for the manufacture of acetates by conventional means. In our opinion, the primary reasons are due to the inherent low-purity of the finished Tigney pulp.

Some examples of major operating problems expected with the Tigney pulp are given below:

High Values	Example Major Problems
S_{18}	High haze in the acetate solution (indicative of unreacted material) High false viscosity (increased pumping requirements) Low filterability
Extractives	High colour in finished plastic product
Ash	Reduced filterability
Calcium	High false viscosity

High and variable metal ion content could neutralize a portion of the sulphuric acid catalyst leading to incomplete acetylation reaction. High brightness pulp is required for attaining good yarn and plastic colour (29,34).

Microcrystalline Cellulose

The original patented technology involves acid hydrolysis of amorphous cellulosic fractions of high-purity wood pulp and subsequent mechanical disintegration of the purified pulp to form an inert microcrystalline product (53-55). The basic requirements of the starting pulp include high and stable brightness, and low content of extraneous substances (such as extractives, metals and ash). Commercial microcrystalline cellulose product has a relatively low DP (known commonly as the level-off DP). Microcrystalline cellulose is manufactured principally for use in the food and pharmaceutical industries (54-57).

Pazner (58) has prepared lab samples of micro-crystalline cellulose from the Tigney cellulose after it has been bleached in two stages with ClO_2 and H_2O_2. The final pulp brightness was 83 to 89 pts.

A high (ca. 91%) alpha-cellulose content of the finished Tigney pulp has been cited by Pazner (58) to be an important advantage. This figure is somewhat higher than those reported by other contractors (30,31,39). This discrepancy might be attributable to the general difficulty ecountered by Pazner and others in filtering the alkali-reacted cellulose

during the chemical analysis. The non-uniformity of the Tigney cellulose sample may also have been a contributing cause (60).

The microcrystalline cellulose product prepared by Pazner was noted to be deficient in brightness and brightness stability (58). In our opinion, these problems might be due in part to the residual extractives and the carbonyl groups (on the cellulose) present in the ClO_2-H_2O_2 bleached pulp. At least in previous analysis (31), the Copper number (indicative of the carbonyl content) of the finished Tigney pulp was relatively high in comparison to commercial dissolving pulp. Unfortunately, no analysis of carbonyl or extractives contnent was made on the ClO_2/H_2O_2 bleached pulp. Moreover, the high extractives content in the starting pulp could deposit undesirably on operating equipment during the acid (HCl) hydrolysis step (33).

On the basis of sugar analysis of the Tigney cellulose, Pazner (60) suspected that the ultimate yield of Tigney cellulose might be very low, possibly approaching the yield of conventional dissolving pulp.

Battista has also evaluated the qualitative characteristics of microcrystalline cellulose made from the Tigney cellulose (61). The observation made was that it might be possible to produce a non-food/non-pharmaceutical grade from the Tigney cellulose (hypochlorite-bleached only).

However, Battista had expressed some concern about the apparent low starting DP of the Tigney cellulose. The value is already very close to the level-off DP of the microcrystalline product. There was little or no range to regulate the uniformity of the required DP. Battista was not able to comment on the effect of trace metal ions, extractives and hemicelluloses on the yield and quality of microcrystalline cellulose product. The normal approach in the production of microcrystalline cellulose is to start with a high purity dissolving wood pulp.

Non-dissolving Pulp

Suggested alternative usage of the Tigney cellulose fraction as a filler pulp is interesting but not very practical. For this purpose, production of aspen refiner pulp may be simpler and cheaper than the Tigney approach. Certainly the refiner pulp would have much higher yield.

As shown in Table III, the Tigney cellulose consists of mostly "fines". Physical strength of paper made with the Tigney cellulose would be very low (14) as compared to conventional bleached aspen kraft pulp. The expected low drainage of the Tigney cellulose could be a serious problem.

Table III. Fibre Classification of Tigney Cellulose

		Tigney Cellulose (30)	Typical Bleached Aspen Kraft (62)
Bauer-McNett, % retained on	14 mesh		0.4
	16 mesh	<0.05	
	28 mesh		6.4
	30 mesh	0.13	
	48 mesh		37.6
	50 mesh	17.4	
	100 mesh	24.3	40.5
% through	100 mesh	58.2	15.1

For the production of fluff pulp, certain fibre coarseness and resiliency are required. Both of these parameters are closely correlated to the long-fibre content of pulp (63). Because of its exceptionally high "fines" content, the Tigney cellulose would not be acceptable for the production of fluff-grade pulp. Johnson & Johnson (64) did not find the Tigney cellulose to be unsuitable for "fluff" product usage. Bialski (30) has also made a similar conclusion.

NON-CELLULOSE PRODUCTS

In the Tigney processing scheme described in Figure 4, there are three successive processing steps used for the isolation of non-cellulose components from the steam exploded raw pulp mass. The specific steps are: water, followed with ethanol, and finally with dilute NaOH.

Step I Water Extraction

Acetic acid, xylose, xylose oligomers, and simple monomeric compounds (e.g., vanillan, syringaldehyde, furfural and methyl furfurals) were reported to be removed by water extraction of the raw pulp (21). As expected, there were also numerous unidentified chemical components in the water extract.

Tigney reported that about 18 to 30% of the initial raw pulp (dry basis) would be separated in this fraction, with a processing time of ranging from 80 to 11 seconds respectively (21). With the exception of acetic acid (about 30 kg/oven-dry tonne of raw pulp), quantitative estimates of specific product yields were not made. No precise data were available to estimate the specific amount of water used for this operation. Without these vital data, it would be impossible to determine the technical and economic viability of recovering the high-value

products (e.g., vanillan and furfural) from the water extract. Although there are many known separation techniques available for the recovery of these chemical compounds, their economic practicality can not be assumed in this situation.

Step II Ethanol Extraction

Alcohol-soluble lignin and additional simple phenolic compounds (e.g., vanillan and syringaldehyde) are isolated in this step. On the basis of the raw Tigney pulp, 5 to 23% of the original (dry-basis) material would be removed at this step, with a processing time ranging from 11 to 80 seconds, respectively (21). The lignin solubility trend was monotonic. Based on the work of Lora and Wayman (10), a lignin solubility curve with a maximum value would have been expected (See also Figure 1).

Several lignin sub-fractions were prepared and evaluated (21). The number-average molecular weight of lignin material isolated in the ethanol extract was reported to be in the range of 700 to 1200. As a comparison, Chua and Wayman (11) reported the number-average molecular weight of dioxane-extracted lignin (from aspen autohydrolysis at 195° C and 5 minutes) to be about 1320. Their experimental data suggest that shorter cook time would give lower number-average molecular weight lignin material. This alcohol-soluble lignin from steam-explosion process has generally been expected by various researchers to be very reactive chemically (9-14).

Certain amounts of unsaturated fatty acid (e.g., linoleic acid) and phytosterols (e.g., beta-sitosterol) have also been detected in the ethanol fraction. The presence of these compounds are not unexpected as these compounds are known to be present in aspen wood (7). However, linoleic acid might be an artifact of the precursor triglycerides. It is now suspected that during the methylation of the ethanol-extract for gas chromatography, the triglycerides present were inadvertently causticized with the NaOH present in the methylating reagent ("Methelute"). This reaction with NaOH would result in the formation of "free" fatty acids which are immediately methylated in situ (65). Little or no free fatty acids are known to be present in the living hardwood or softwood tree.

In the most recent process configuration, this ethanol extraction after the initial water extraction is omitted (22,24). The water extracted is immediately extracted with a dilute NaOH solution. Without this extraction step, the entire "wood chemicals" factory scheme could be simplified. However, the availability "chemically reactive" lignin material might thus be eliminated.

Step III NaOH Extraction

The final extraction is with dilute NaOH solution (22,23). Xylan and related oligomers, and alkali-soluble lignin are recovered in this fraction. The total yield of the NaOH extraction step (0.2% and 5% NaOH) ranged from 5 to 12%, based on raw oven-dry pulp. The highest amount of

NaOH-extract was obtained with the shortest (ca. 11 seconds) processing time (21).

Without the ethanol extraction step, the maximum recoverable substances in a single NaOH extraction would probably be the sum of (preceding) ethanol extract plus (above) NaOH extract.

Xylose and Xylos Derivatives

To date, only small amounts of xylose and furfural have been isolated in pure form on a laboratory scale (21). Using known chemical procedures, Tigney also prepared some xylitol from a xylose mixture recovered from the water extract. The practical significance of these lab-scale separation and preparation methods is somewhat limited.

Lignin Material

Two types of Tigney lignin were sent by AFS to various contractors. The specific samples were 1) lignin recovered in the NaOH extraction of water pre-extracted/alcohol-extracted pulp (Type A) and 2) lignin recovered in the alcohol extraction of water-extracted pulp (Type B).

General Characteristics

At Virginia Polytechnic Institute, Glasser has determined the general characteristics of the Tigney lignin (Type A) material. A glass transition temperature of 95° C was observed. This value was considered to be normal for many organosolv and steam explosion type lignin (66,67). In contrast, the glass transition temperature of native wood lignin is generally recognized to be in the range of 150 to 170° C (17). Interestingly, Glasser et al (67) had reported the glass transition temperature of steam-explosion lignin (from Iotech Corp.) to be in the range of 133-139° C. From the additional examination of the phenolic content and molecular weight distribution, Glasser concluded that the Tigney lignin is basically similar in nature to other normal hardwood steam explosion (or autohydrolysis) lignin (66).

Reed Inc. has also analyzed the various chemical constituents in two samples of Tigney lignin (68). The ash content of both lignin samples were determined to be the same level (ca. 1%) as that of typical ammonium base lignosulphonate (66). The methoxyl content (ca. 18%) appeared to be twice as high as many commercial lignosulphonates. Generally the reactive of the lignin (as a phenolic resin, for example) is hindered by, among other things, methoxyl groups and the aliphatic side chains. Resin properties are unusually improved by demethylation, thereby increasing the active phenol content (17).

Moreover, the reducing bodies (reflecting the presence of monomeric sugars) are likened to many unrefined commercial lignosulphonates. For many dispersing applications, it is generally recognized that the lignin material has to be rendered sugar-free (17,69-72). Stone (68) thought

that the Tigney lignins might find application in phenolic resin extension. But no tests were actually conducted to establish their acceptance.

Brazny studied the reactivity of the two types of Tigney lignin towards formaldehyde (73). This test was conducted to assess the ultimate applicability of these lignins in the preparation of acceptable lignin-formaldehyde resins. As shown in Figure 5, the reactivity of the two Tigney lignins were substantially less than the kraft softwood or aspen organosolv lignins. Note the similar reactivity of Tigney Lignin A and Tigney Lignin B. This finding suggests that the Tigney lognins do not possess unusual chemical reactivity.

Cyr and Laidler investigated some characteristics of lignins from the Tigney exploded wood process (74). These workers noted that the molecular weight distributions were very different for lignins prepared in alcohol and NaOH solutions. Alkali-soluble lignin contained more high molecular weight material than alcohol-soluble lignin. A "drying oil" (up to 5% of raw pulp; probably mostly unsaturated fatty acids) was observed in the alcohol extracted fraction. This "drying oil" was noted to undergo polymerization via an auto-oxidation mechanism at room temperature. This finding led these workers to suggest that the "age" of the extracted lignin material has a profound influence on the ultimate properties of the isolated lignin.

Diesel Fuel Additive

The proposed concept is to use the Tigney lignin (Type B) as a "bridging" chemical for the blending of methanol to diesel fuel. Although there is no scientific basis for this approach, it has been deemed worthy of test because of the unusual solubility of the Tigney lignin in common organic solvents. Djordjevic and Douglas (75) have investigated the use of organosolv (hardwood) lignin as a fuel extender. The lignin product was added to a mixture of butanol and diesel fuel. Some filtration problems were encountered with the partial precipitation of lignin by the diesel fuel.

Ocelet Chemicals has found the Type B Tigney lignin to be only 85% soluble in methanol (76). The insoluble 15% material was noted to be gum-like and to stick to the wall of the test apparatus. This substance would appear to be related to the "drying oil" cited previously by researchers at ARC (74). At present, it is not clear if this sticky insoluble material could readily removed from the bulk lignin. Whether the Tigney (Type B) lignin can act as a "bridging or emulsifying" agent remains untested.

Composite Board Adhesive

The biggest potential usage of the Tigney lignin is the replacement of phenol in the formulation of standard phenol-formaldehyde (PF) resins. Over the past 50 years, there have been numerous attempts to develop a satisfactory wood adhesive from lignin (77). Success have been limited.

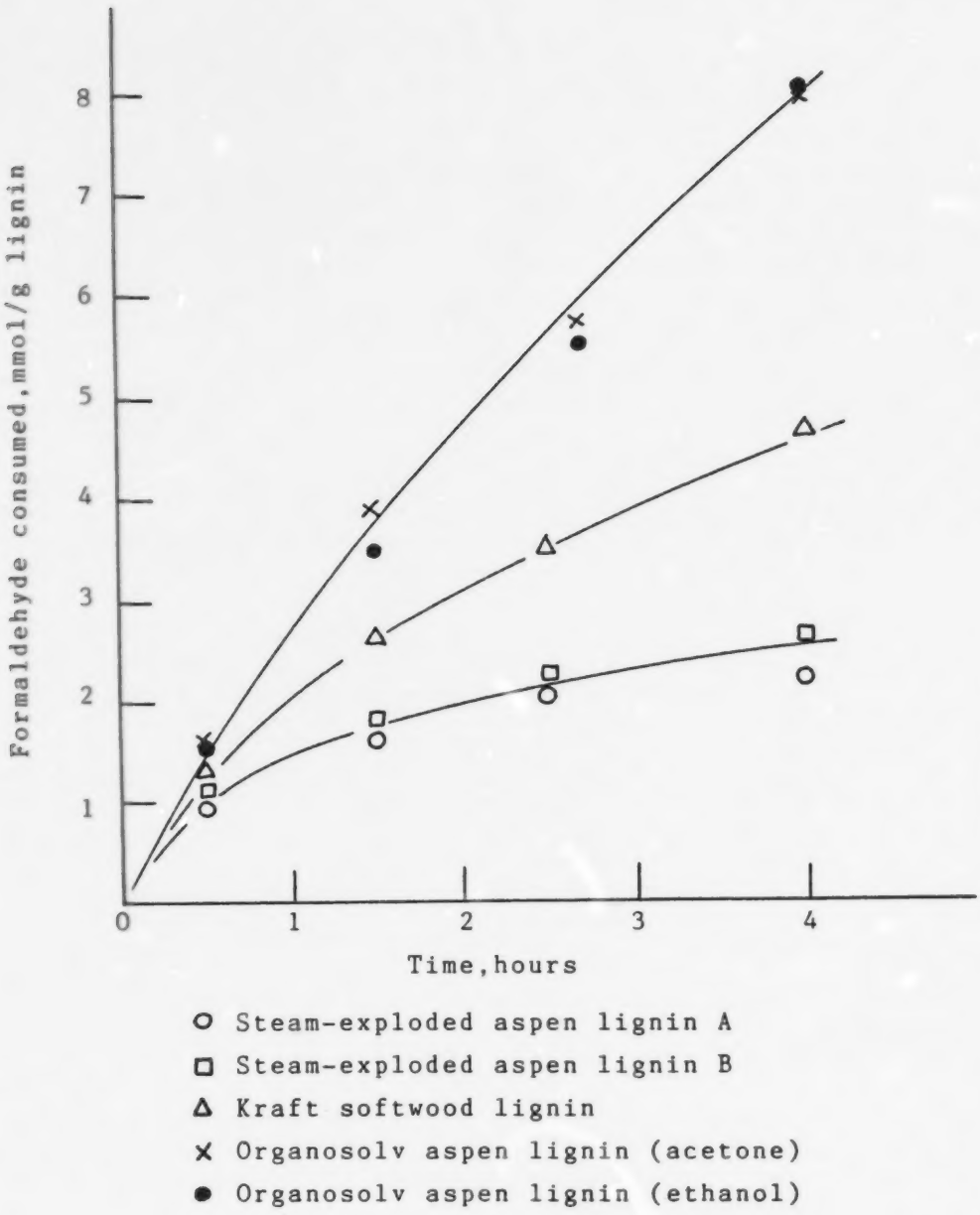


Figure 5 - Consumption of Formaldehyde by Lignins in Hydroxymethylation [73]

A sample of Tigney lignin was evaluated by Bakelite Thermosets Ltd. (78). The reactivity of the Tigney lignin with formaldehyde was observed to be very low in comparison to other commercial (refined) lignin products. The as-received product was rejected as an acceptable phenol substitute.

Separately, workers at ARC have evaluated the use of Tigney lignins in the preparation of waferboard (79). An additional sample of alkali-extracted (Tigney) lignin made from the steam-exploded processing of Pelican OSB residues was also evaluated (80).

Preliminary test results indicated that the Tigney lignins do have certain adhesive properties. Bach et al. commented that Type B (alcohol) lignin appeared to be slightly better than Type A (alkali) lignin in adhesion properties. In any case, under dry test conditions, both Tigney lignins were tested to have less than 20% of the bonding strength of the reference PF resin. Any amount of Tigney lignin substitute was observed to decrease the base-line properties of the standard PF board. Moreover, at the 20% substitution level, the swelling properties and the bond durability begin to deteriorate markedly. The test results with the Tigney lignin made from Pelican OSB residues were also unsatisfactory.

Bach et al. have suggested that longer curing time and possibly high curing temperature might render the performance of the Tigney lignin to be comparable to the PF resin (79). But the plant economics would then become unacceptable with reduced productivity and higher energy cost.

Gardener and Sellers (81) has tested a lignin extender made by the alkali-extraction of Masonite pulp (steam-explosion conditions: 225° C, 450 psig and 60 seconds). Plywood was chosen as the substrate for testing. Test results indicated that the plywood shear strength made with steam-exploded lignin adhesives (up to 30% substitution) were at least as good as those with the PF control. Wood failure of the lingin-based plywood was significantly lower than the control. Moreover, lignin-based adhesive appeared to very sensitive to assembly time, resulting in undercure or dry-out appearance. These results confirmed that the generic steam-explosion process could produce a lignin of limited adhesive value. Its full usage is still not ascertained.

With the advent of an improved binderless panelboard (82), the commercial prospect of the Tigney lignin as a "low-cost" adhesive for the panel board industry would be limited.

In our opinion, even if the overall economics of the Tigney lignins were very favourable, the somewhat poor technical performance of the Tigney lignin relative to the standard PF resin would not be acceptable to the panelboard industry.

Drilling Mud Application

Georgia-Pacific Corp. (Bellingham, WA) has tested the performance of the Tigney lignin against samples of conventional calcium

lignosulphonate (Lignosite) and chrome lignosulphonate (Q-Broxin ?) (83). The standard API mud viscosity test (84) was made with Gulf mud contaminated with gypsum and salt water. In comparison to the reference chrome-lignosulphonate, the Tigney lignin gave:

* higher initial gel strength
* higher yield point (shear stress required to initiate flow)
* higher fluid loss

Interestingly, the plastic viscosity of the Tigney lignin-added mud was lower than that of the reference product. Plastic viscosity is shear stress required to induce a unit change in shear rate. This parameter is of considerable importance in regulating the rheology of non-Newtonian fluids such as drilling mud.

Because specific geologic conditions of the drill holes require different properties of drilling mud, the only suitable comparison is to test the new lignin product against a well-established product for a given standard mud. On this basis, the Tigney lignin was considered unacceptable as a satisfactory replacement for the commercially available lignin products (83).

PROCESS ECONOMICS

The Celpap (85) assessment of market economics might be overly optimistic. It is true that alternative sources of dissolving pulp (86-88) and phenols are being sought in Europe. The demand for dissolving might be met by incremental capacity expansion of many existing plants. For example, Saicor in South Africa is implementing a further addition of 100,000 tonnes of pine dissolving pulp by 1988.

The conventional dissolving pulp quality is significantly higher than that easily achieved with the simple Tigney pulp. In some instances, it might be possible that modifications of in-place commercial manufacturing plant operations could be made to accommodate the "lower-grade" Tigney pulp. In our opinion, this scenario might be somewhat unrealistic. Despite the apparent advantage of using a lower-cost cellulose raw material, major changes of established processing techniques in existing manufacturing plants are very difficult to achieve. Follow-up purification of the Tigney cellulose would certainly increase the complexity and cost of operation, and quite likely reduce the overall product yield.

In the case of wood as chemical feedstock, previous studies at PPRIC (89) and elsewhere (90-92) have shown that non-conventional "wood chemicals" factory would have great difficulties in competing against chemical feedstock from traditional source (even during the days of high and rising petroleum prices). The principal problems are 1) the requirements of high yields and qualities of all fractions recovered from the wood raw material, and 2) the exceptional complexity of marketing all derived chemical products simultaneously.

Furthermore, the problems of successful new product development to displace present products, and eventual market accessibility of the new products are frequently underestimated. It is insufficient (and misleading) to simply multiply "product required" by the "value of the product" to obtain the market potential.

It would appear that complete marketability of all three Tigney fractions for high values is needed to justify the establishment of such a "wood chemical" manufacturing operation in Alberta. This marketing feat is not easy to accomplish.

In the best-case scenario at least one lead high-volume product is needed to sustain the viability of the "wood chemicals" factory. But no Tigney product has emerged to meet the minimum technical performance criteria.

CONCLUSIONS

A detailed review of available information on the Tigney technology and its cellulose and lignin products have been completed. The major conclusions are as follows:

1. The steam-explosion process is capable of producing only impure fractions of cellulose, hemicellulose and lignin. Because of very nature of wood/wood components and of the Tigney (or any other similar) process, optimization of operating conditions to produce three "pure" fractions concurrently is not possible.

2. The quality of the Tigney cellulose was concluded to be unsatisfactory for the preparation of viscose, acetate or microcrystalline products. It is unlikely that the Tigney cellulose in its present quality could displace conventional dissolving pulp for these end uses.

3. The chemical reactivity of the Tigney lignin was noted to be surprisingly low. Moreover, the chemical characteristics of the Tigney lignin does not appear to be unique. It is similar to other steam-explosion (or autohydrolysis) hardwood lignin material.

4. The Tigney lignin product has been tested to be unacceptable for use as direct substitute for phenol-formaldehyde resin for panelboards, bridging agent for methanol-diesel fuel mixture and drilling mud additive.

5. The addition of any subsequent purification steps would only increase the immense complexity of the concept of producing low-cost valuable chemical products from aspen wood. The economic viability is dependent, to a large extent, on the successful marketing of many wood-derived products simultaneously.

RECOMMENDATIONS

Tigney cellulose and lignin have not been demonstrated to meet the minimum technical performance of products which they are intended to replace. The prospect of success is not good on the basis of present scientific and technical evidence. Further pilot plant development work is not justified at this time.

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